

## Supporting Information

*belonging to*

### **Organization of spin- and redox-labile metal centers into Langmuir and Langmuir-Blodgett films**

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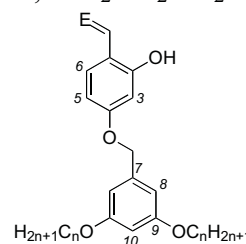
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## 1. Synthetic details

**Synthesis of 3e.** A suspension of 2,4-hydroxybenzaldehyde (1.40 g, 10.1 mmol), KI (328 mg, 2.0 mmol) and NaHCO<sub>3</sub> (1.08 g, 12.8 mmol) in MeCN (140 mL) was stirred at 70 °C during 15 min. A warm solution of corresponding benzyl bromide **2e** (4.0 g, 9.4 mmol) in dry THF (60 mL) was slowly added and stirring at reflux was continued for 3 d. The formed precipitate was filtered and washed with THF. The combined filtrates were evaporated *in vacuo* and the residue was purified by gradient column chromatography (SiO<sub>2</sub>, hexane to hexane/EtOAc 9:1). The title compound was obtained as a yellow oil (3.87 g, 85%). Upon standing some white crystals formed, which were collected, washed with EtOH and dried *in vacuo*. M.p. 42 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz): δ 11.46 (s, 1H, OH), 9.72 (s, 1H, CHO), 7.44 (d, 1H, *J* = 8.7 Hz, C<sup>6</sup>H), 6.61 (d, 1H, *J* = 8.7 Hz, C<sup>5</sup>H), 6.52 (s, 2H, C<sup>8</sup>H), 6.49 (s, 1H, C<sup>3</sup>H), 6.41 (m, 2H, C<sup>10</sup>H), 5.03 (s, 2H, C<sup>ar</sup>CH<sub>2</sub>O), 3.93 (t, 4H, *J* = 6.3 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 1.76 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 1.5–1.4 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.4–1.2 (m, 16H, all CH<sub>2</sub>), 0.88 (t, 6H, *J* = 6.7 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 90 MHz): δ 194.6 (CHO), 166.0, 164.6 (2 × C<sup>ar</sup>O), 160.8 (C<sup>9</sup>), 137.9 (C<sup>7</sup>), 135.4 (C<sup>6</sup>H), 115.5 (CCHO), 109.1 (C<sup>5</sup>H), 105.8 (C<sup>8</sup>H), 101.8 (C<sup>3</sup>H), 101.1 (C<sup>10</sup>H), 70.5 (OCH<sub>2</sub>C<sup>ar</sup>), 68.2 (OCH<sub>2</sub>), 32.5–29.0, 22.8 (all CH<sub>2</sub>), 29.5 (OCH<sub>2</sub>CH<sub>2</sub>), 26.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). HR–MS (ESI, Acetone): Calcd. for C<sub>30</sub>H<sub>43</sub>O<sub>5</sub> [M – H]<sup>–</sup> *m/z* = 483.3116, found *m/z* = 483.3105. Anal. found (calcd) for C<sub>30</sub>H<sub>44</sub>O<sub>5</sub> (484.68): C 74.41 (74.34); H 9.17 (9.15)



**Synthesis of 3f.** According to the method described for **3e**, a suspension of 2,4-hydroxybenzaldehyde (1.26 g, 8.9 mmol), KI (296 mg, 1.8 mmol) and NaHCO<sub>3</sub> (974 mg, 11.6 mmol) in MeCN (125 mL) was reacted with **2f** (3.61 g, 6.7 mmol) in THF (60 mL). The title compound was obtained as a white solid (2.15 g, 54%). M.p. 60 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 11.46 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.43 (d, 1H, *J* = 8.7 Hz, C<sup>6</sup>H), 6.60 (dd, 1H, *J* = 8.7, 2.3 Hz, C<sup>5</sup>H), 6.52 (d, 2H, *J* = 1.8 Hz, C<sup>8</sup>H), 6.49 (d, 1H, *J* = 2.4 Hz, C<sup>3</sup>H), 6.41 (t, 2H, *J* = 2.3 Hz, C<sup>10</sup>H), 5.02 (s, 2H, C<sup>ar</sup>CH<sub>2</sub>O), 3.93 (t, 4H, *J* = 6.6 Hz, CH<sub>2</sub>CH<sub>2</sub>O), 1.81–1.71 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 1.49–1.39 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.39–1.19 (m, 32H, all CH<sub>2</sub>), 0.88 (t, 6H, *J* = 7.0 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 194.6 (CHO), 166.0, 164.6 (2 × C<sup>ar</sup>O), 160.8 (C<sup>9</sup>), 137.9 (C<sup>7</sup>), 135.4 (C<sup>6</sup>H), 115.8 (CCHO), 109.1 (C<sup>5</sup>H), 105.8 (C<sup>8</sup>H), 101.8 (C<sup>3</sup>H), 101.1 (C<sup>10</sup>H), 70.5 (OCH<sub>2</sub>C<sup>ar</sup>), 68.2 (OCH<sub>2</sub>), 32.1–29.0, 22.8 (all CH<sub>2</sub>), 29.5 (OCH<sub>2</sub>CH<sub>2</sub>), 26.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). MS (ESI): *m/z* = 619.4 [M + Na]<sup>+</sup>. Anal. found (calcd) for C<sub>38</sub>H<sub>60</sub>O<sub>5</sub> (596.88): C 76.36 (76.47); H 10.22 (10.13).

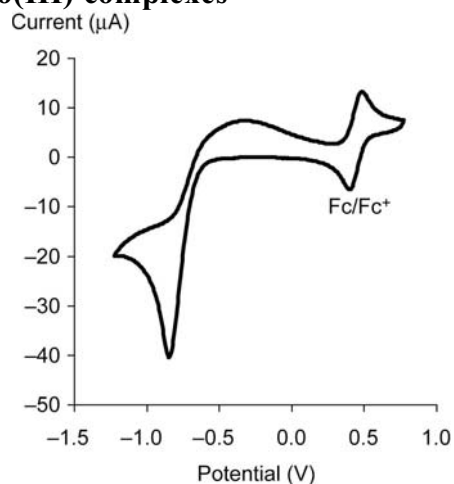
**Synthesis of 3g.** According to the method described for **3e**, a suspension of 2,4-hydroxybenzaldehyde (2.27 g, 16.1 mmol), KI (534 mg, 3.2 mmol) and NaHCO<sub>3</sub> (1.76 g, 20.9 mmol) in MeCN (460 mL) was reacted with **2g** (8.54 g, 12.1 mmol) in THF (200 mL). After filtration of the reaction mixture, the combined filtrates were concentrated to ca. 150 mL and stored at 4 °C for 1h. A precipitate formed, which was collected, washed with EtOH, and dried *in vacuo* to give **3g** (6.78 g, 73%). M.p. 73 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 11.45 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.43 (d, 1H, *J* = 8.7 Hz, C<sup>6</sup>H), 6.60 (dd, 1H, *J* = 8.7, 2.3 Hz, C<sup>5</sup>H), 6.52 (d, 2H, *J* = 1.8 Hz, C<sup>8</sup>H), 6.49 (d, 1H, *J* = 2.3 Hz,

C<sup>3</sup>H), 6.41 (t, 2H,  $J = 2.3$  Hz, C<sup>10</sup>H), 5.02 (s, 2H, C<sup>ar</sup>CH<sub>2</sub>O), 3.93 (t, 4H,  $J = 6.6$  Hz, CH<sub>2</sub>CH<sub>2</sub>O), 1.81–1.71 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 1.49–1.39 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.39–1.19 (m, 56H, all CH<sub>2</sub>), 0.88 (t, 6H,  $J = 7.0$  Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  194.6 (CHO), 166.0, 164.6 (2  $\times$  C<sup>ar</sup>O), 160.8 (C<sup>9</sup>), 137.9 (C<sup>7</sup>), 135.4 (C<sup>6</sup>H), 115.8 (CCHO), 109.1 (C<sup>5</sup>H), 105.8 (C<sup>8</sup>H), 101.8 (C<sup>3</sup>), 101.1(C<sup>10</sup>), 70.5 (OCH<sub>2</sub>C<sup>ar</sup>), 68.2 (OCH<sub>2</sub>), 32.1–29.0, 22.8 (all CH<sub>2</sub>), 29.5 (OCH<sub>2</sub>CH<sub>2</sub>), 26.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). MS (ESI):  $m/z = 763.7$  [M – H]<sup>–</sup>. Anal. found (calcd) for C<sub>50</sub>H<sub>84</sub>O<sub>5</sub>: C 78.51 (78.48); H 11.07 (11.06)

**Synthesis of 4c.** To a solution of **3c** (2.24 g, 7.3 mmol) in warm EtOH (150 mL) were added MgSO<sub>4</sub> (2.90 g, 24.1 mmol) and triethylenetetramine (0.55 mL, 3.65 mmol). The mixture was stirred at reflux for 16 h under an Ar atmosphere. Subsequently the precipitate was rapidly filtered, rinsed with EtOH (3  $\times$  10 mL) and the combined filtrates were concentrated to 40 mL. Upon cooling to –25°C a precipitate slowly formed, which was collected by filtration, washed with cold EtOH (3  $\times$  30 mL) and dry Et<sub>2</sub>O (2  $\times$  30 mL). After drying *in vacuo*, **4c** was obtained as an off-white solid (1.30 g, 49%). M.p. 118–121 °C. IR (CHCl<sub>3</sub>): 1632 (C=N), 1605 cm<sup>–1</sup> (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz):  $\delta$  8.08 (s, 2H, N=CH), 6.93 (d, 2H,  $J = 8.6$  Hz, C<sup>6</sup>H), 6.19 (d, 2H,  $J = 2.2$  Hz, C<sup>3</sup>H), 6.04 (dd, 2H,  $J = 8.6, 2.3$  Hz, C<sup>5</sup>H), 4.09–3.95 (m, 2H, CH<sub>2</sub>N=), 3.88 (t, 4H,  $J = 6.7$  Hz, OCH<sub>2</sub>), 3.41–3.24 (m, 4H, CH<sub>2</sub>N= and CH<sub>2</sub>CH<sub>2</sub>N=), 2.91–2.78 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>N), 2.57–2.37 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>N= and NCH<sub>2</sub>CH<sub>2</sub>N), 1.92 (s, 2H, NH), 1.83–1.55 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.46–1.35 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35–1.12 (m, 56H, CH<sub>2</sub>), 0.87 (t, 6H,  $J = 6.7$  Hz, CH<sub>3</sub>), OH not resolved. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  172.5, 164.0 (2  $\times$  C<sup>ar</sup>O), 167.1 (N=CH), 135.5 (C<sup>6</sup>H), 115.3 (CCHN), 105.2 (C<sup>5</sup>H), 102.6 (C<sup>4</sup>H), 67.6 (OCH<sub>2</sub>), 55.8 (CH<sub>2</sub>N=), 47.4 (CH<sub>2</sub>CH<sub>2</sub>N=), 44.4 (NCH<sub>2</sub>CH<sub>2</sub>N), 32.0, 30.0–29.3, 22.8 (all CH<sub>2</sub>), 29.4 (OCH<sub>2</sub>CH<sub>2</sub>), 26.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). HR–MS (ESI): calcd for C<sub>44</sub>H<sub>75</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup>  $m/z = 723.5783$ , found  $m/z = 723.5783$ .

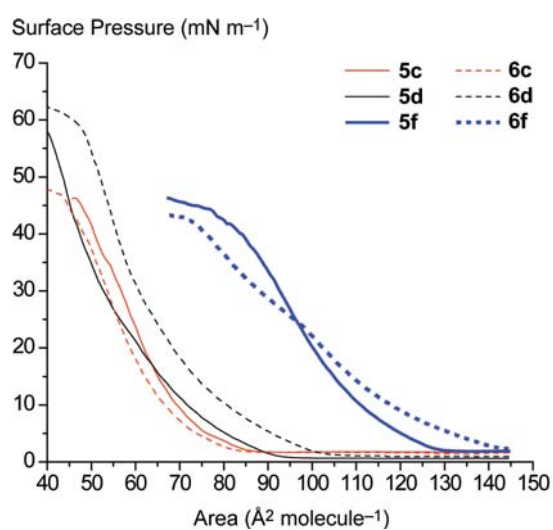
**Synthesis of 4d.** A solution of **3d** (3.27 g, 8.37 mmol) in warm EtOH/THF 2:1 (60 mL) was added to a suspension of triethylenetetramine (612 mg, 4.18 mmol) and MgSO<sub>4</sub> (3.00 g) in EtOH (60 mL). The mixture was heated to reflux for 16 h under Ar and subsequently filtered. The residue was rinsed with EtOH (2  $\times$  30 mL) and the product was extracted from the filter with THF (3  $\times$  75 mL) to give, after evaporation of the solvent, the pale yellow solid **4d** (2.51 g, 67%). M.p. 122–124 °C. IR (CHCl<sub>3</sub>): 1634 (C=N), 1605 cm<sup>–1</sup> (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz):  $\delta$  8.07 (s, 2H, N=CH), 6.92 (d, 2H,  $J = 8.6$  Hz, C<sup>6</sup>H), 6.19 (d, 2H,  $J = 2.2$  Hz, C<sup>3</sup>H), 6.03 (dd, 2H,  $J = 8.6, 2.3$  Hz, C<sup>5</sup>H), 4.09–3.95 (m, 2H, CH<sub>2</sub>N=), 3.88 (t, 4H,  $J = 6.6$  Hz, OCH<sub>2</sub>), 3.41–3.24 (m, 4H, CH<sub>2</sub>N= and CH<sub>2</sub>CH<sub>2</sub>N=), 2.93–2.76 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>N), 2.59–2.35 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>N= and NCH<sub>2</sub>CH<sub>2</sub>N), 1.90 (s, 2H, NH), 1.80–1.65 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.50–1.35 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35–1.12 (m, 56H, CH<sub>2</sub>), 0.88 (t, 6H,  $J = 6.7$  Hz, CH<sub>3</sub>), OH not resolved. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 90 MHz):  $\delta$  172.5, 164.1 (2  $\times$  C<sup>ar</sup>O), 167.1 (N=CH), 135.6 (C<sup>6</sup>H), 115.3 (CCHN), 105.2 (C<sup>5</sup>H), 102.6 (C<sup>3</sup>H), 67.6 (OCH<sub>2</sub>), 55.8 (CH<sub>2</sub>N=), 47.4 (CH<sub>2</sub>CH<sub>2</sub>N=), 44.5 (NCH<sub>2</sub>CH<sub>2</sub>N), 32.1, 30.2–29.8, 22.8 (all CH<sub>2</sub>), 29.7 (OCH<sub>2</sub>CH<sub>2</sub>), 26.2 (OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). Anal. found (calcd) for C<sub>56</sub>H<sub>98</sub>N<sub>4</sub>O<sub>4</sub> (891.76)  $\times$  MgSO<sub>4</sub>: C 66.30 (66.48); H 9.66 (9.76); N 5.64 (5.54). HR–MS (ESI): calcd for C<sub>56</sub>H<sub>99</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup>  $m/z = 891.7661$ , found  $m/z = 891.7664$ .

## 2. Representative CV of Co(III) complexes

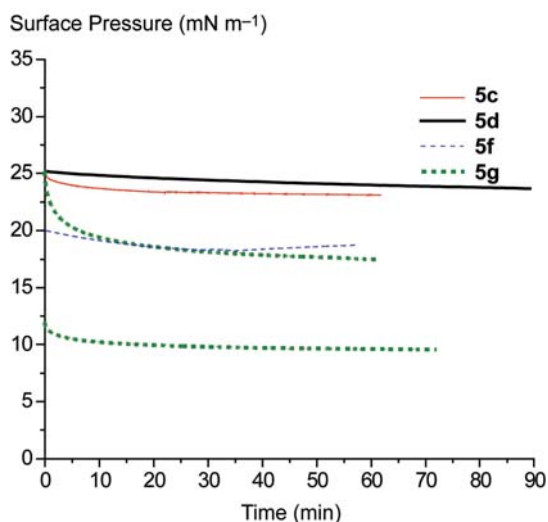


**Figure S1.** Representative cyclic voltammogram of complex **6d** indicating the irreversible reduction of the cobalt center.

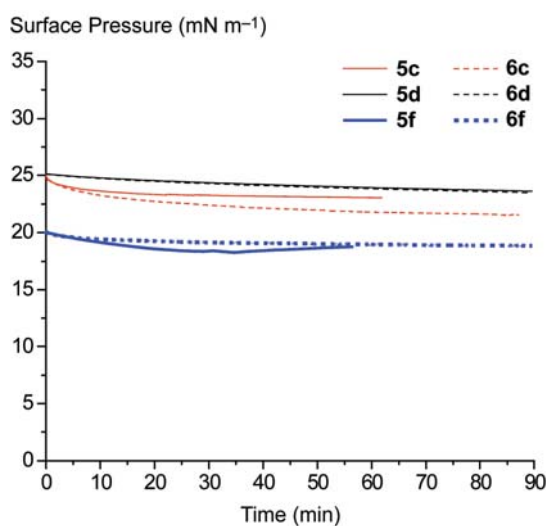
## 3. Langmuir film characteristics



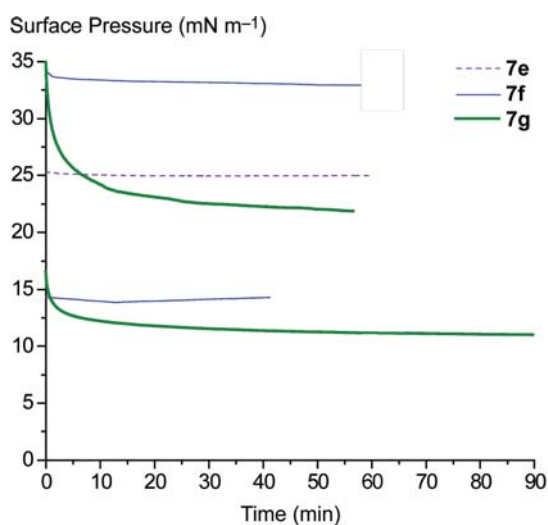
**Figure S2.** Representative pressure-area isotherms for the cobalt complexes **5c**, **5d**, and **5f** containing a  $\text{Cl}^-$  anion, and for the analogous complexes **6c**, **6d**, and **6f** containing a  $\text{NO}_3^-$  anion.



**Figure S3.** Film stability deduced from the time-dependent pressure change at a fixed area.

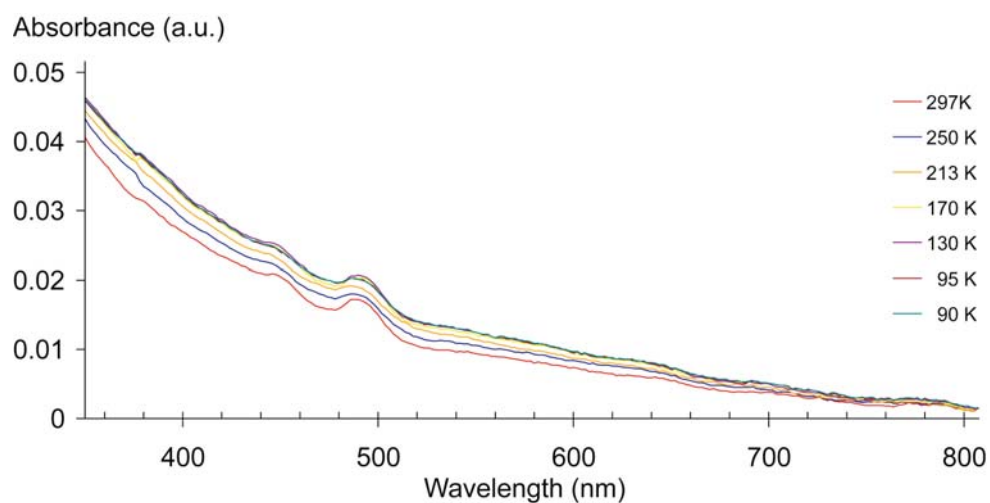


**Figure S4.** Stability of films comprising cobalt complexes comprising Cl<sup>-</sup> (**5**) and NO<sub>3</sub><sup>-</sup> (**6**) anions, respectively, as deduced from the time-dependent pressure change at a fixed area.



**Figure S5.** Time-dependent change of the surface pressure at a fixed area, indicating the different stability of films composed of iron complexes **7e–g** at different initial compression.

#### 4. UV-vis measurement of bilayer LB film



**Figure S6.** Superimposed absorption spectra of bilayers of complex **7d** in the visible range, illustrating a change in adsorption in the 250-170 K range. Addition of further layers is prevented by the partial desorption of the second layer, thus leading to a maximum coating of two complete layers on the support (cf. transfer ratios, Table 2 and Fig. 6 in the article).